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## DIRECT MEASUREMENTS OF THE MAGNETOCALORIC EFFECT

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**ABSTRACT** — We present an experimental setup recently developed at DTU Energy Conversion for measuring specific heat and direct isothermal entropy change in a varying magnetic field (DSC device) using calorimetry. The device operates in high vacuum ( $\sim 10^{-6}$  mbar) and measurements are fully automated with respect to magnetic field and temperature control. A magnetic field source comprised of two concentric Halbach type magnets that are fixed with respect to each other through a mechanical gear supply the applied magnetic field. The applied field range is 0.001 to 1.57 T with a minimum field step size smaller than 0.01 T. The magnet control is fully integrated in software allowing measurement scans to be automated. This device is an upgrade of an existing device where it is now possible to install a sample and then run temperature scans at different magnetic fields (specific heat measurement) as well as magnetic field scans under isothermal conditions (direct isothermal entropy change measurements).

### 1. INTRODUCTION

The specific heat of magnetocaloric materials is of crucial importance for characterization, evaluation and generation of property data sets applied in active magnetic regenerator (AMR) models. Having specific heat data as a function of temperature and constant applied magnetic field it is possible to generate entropy curves of a material. This enables the calculation of the magnetocaloric properties, i.e. isothermal entropy change and adiabatic temperature change. Furthermore, in hysteretic materials, heating and cooling specific heat curves are very important for proper handling of the hysteresis in a magnetocaloric context [1].

Differential scanning calorimetry (DSC) is an established technique for measuring specific heat. However, measurements under applied field typically demand custom-built devices [2],[3],[4]. The custom DSC with magnetic field at DTU has been upgraded so it is fully automatic and also a mode for measuring the isothermal entropy change,  $\Delta S$ , has been added. In the following we present the details and the first isothermal entropy change measurements.

### 2. EXPERIMENTAL

The DSC principle relies on two heat flux sensors that are, in principle, identical. These are intimately connected to a thermal reservoir and through this a constant temperature ramp rate may be applied. Placing a sample on one of the heat flux sensors and measuring the difference between the two sensors essentially provides the heat flux through the sample. In practice, we apply Peltier cells where the voltage measured across the cell is proportional to the heat flux through the cell. The key hardware specifics are given in Table I and a schematic of the device is given in Fig. 1.

TABLE I. SPECIFICATIONS OF THE DEVICE. THE THERMAL RESISTANCE IS DERIVED FROM SPECIFICATIONS FROM THE MANUFACTURER.

Hardware	Specification
Heat flux sensors	3.25x4.88 mm Peltier elements OT08,11,F1,0305,11,W2.25, Optotec Thermal resistance approx. 130 K/W
Hall probe	2.5x4x1 mm Arepoc HHP-NU
Temperature measurement	PT-100 elements
Atmosphere	High vacuum ( $\sim 10^{-6}$ mbar)
Temperature	-40 to +55 °C
Magnetic field range	0.001 to 1.57 T

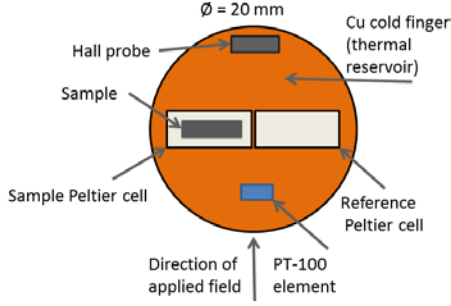


Fig. 1. Schematic of the top of the DSC/direct  $\Delta S$  measurement device.

In any DSC system there will be instrumental hysteresis induced by the lag in temperature between the sample and the thermal reservoir, which in turn is caused by the finite heat transfer across the Peltier cell. Separation of the heating and cooling curves is therefore a (nearly linear) function of temperature ramp rate. This has been calibrated by measuring a standard Ga sample with a melting point at 29.76 °C at different ramp rates and extrapolating to zero ramp rate. We find that at a ramp rate of 1K/min the separation of the curves due to temperature lag is of the order 1 K (device hysteresis). The temperature measurements are corrected for the device hysteresis. Any splitting in peak temperature after this correction is interpreted as intrinsic material hysteresis. In order to convert the measured differential voltage signal to heat flux (and thus either specific heat or entropy change depending on the experiment mode) we use 99.999 wt.% pure Cu as a reference.

The magnetic field source consists of two concentric Halbach-type magnets with the field concentrated in a central axial bore [4]. The magnets are mechanically connected with a gear so that they counter-rotate with exactly the same angular frequency. The direction of the applied field is thus constant while the field magnitude is varied from 0.001 to 1.57 T.

### 3. CONCLUSION

The direct measurement of the isothermal entropy change of a sample of  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  is shown in Fig. 2 and compared to entropy data based on magnetization measured in a vibrating sample magnetometer (VSM), i.e. relying on the Maxwell relation. From these first results it is apparent that the two methods are in agreement. Specific heat measurements show an intrinsic thermal hysteresis of 0.7 K, as discussed in [6].

Our custom made DSC was presented in terms of the recently implemented upgrades. The first results presented show that the method applied to measure direct  $\Delta S$  gives results comparable to those obtained via magnetometry. The advantage of this approach is twofold: i) The same sample may be mounted and specific heat and isothermal entropy change found in one series of experiments and ii) any measurement issues related to the indirect method of using magnetometry may be circumvented by the direct calorimetric method. The latter advantage may prove to be of great importance when studying, e.g., hysteretic effects in magnetocaloric materials especially with a 1<sup>st</sup> order transition.

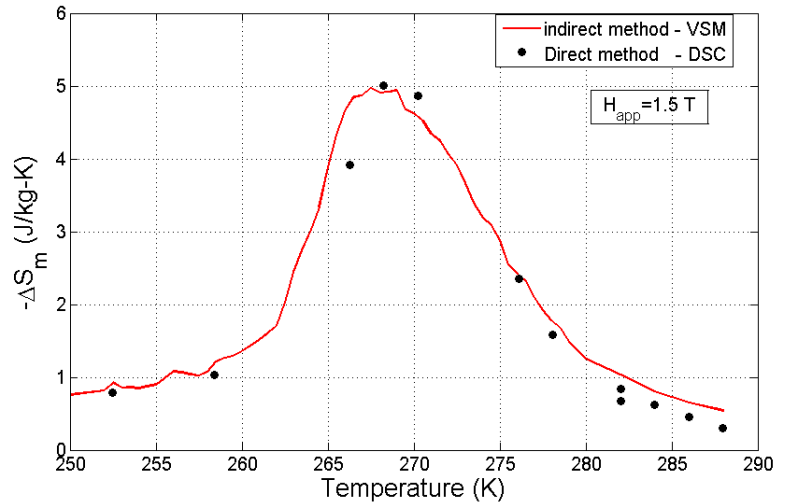


Fig. 2. Direct  $\Delta S$  measurements (symbols) and indirect measurements from magnetization measurements on a sample of  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ . Details about the sample may be found in Ref. [5].

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